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भाग 5 आक्सीकरण–अपचयन विभव अथवा रिडॉक्स विभव

Indian Standard

EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS

PART 5 OXIDATION-REDUCTION POTENTIAL OR REDOX POTENTIAL

ICS 71.040.40

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NEW DELHI 110002

February 1999

Price Group 3

Electronic Measuring Equipment Sectional Committee, LTD 21

FOREWORD

This Indian Standard (Part 5) was adopted by the Bureau of Indian Standards, after the draft finalized by the Electronic Measuring Equipment Sectional Committee had been approved by the Electronics and Telecommunication Division Council.

The objective of this standard is to specify the terminology, definitions, requirements for statements by manufacturers and performance tests for analyzers, sensor units and electronic units used for the determination of redox potential of aqueous solutions.

While preparing this standard assistance has been derived from IEC Pub 746-5 (1992) 'Expression of performance of electrochemical analyzers: Part 5 Oxidation-reduction potential or redox potential' issued by the International Electrotechnical Commission (IEC).

This standard (Part 5) is one of the parts of IS 13673 series of standards on expression of performance of electrochemical analyzers. The other parts of the series are:

Part 1 General

Part 2 *p*H value

Part 3 Electrolytic conductivity

Part 4 Standard for measuring oxygen dissolved in water (*under print*)

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

Indian Standard

EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS

PART 5 OXIDATION-REDUCTION POTENTIAL OR REDOX POTENTIAL

1 SCOPE

This standard (Part 5) is applicable to analyzers, sensor units and electronic units used for the determination of oxidation-reduction or redox potential values of aqueous solutions using relatively inert electron conducting electrodes (for example, platinum or gold). IS 13673 (Part 1) : 1993 'Expression of performance of electrochemical analyzers: Part 1 General', includes further definition of the scope and provides for the general aspects of all electrochemical analyzers. The terms oxidation-reduction potential and redox potential may be used interchangeably.

2 REFERENCES

The Indian Standard listed below is a necessary adjunct to this standard:

IS No.	*Title*
IS 13673 (Part 1) : 1993	Expression of performance of electrochemical analyzers : Part 1 General

3 SYMBOLS AND DEFINITIONS

See **3** of IS 13673 (Part 1) and the following.

3.1 Symbols

a_{red} = reductant ionic activity

a_{ox} = oxidant ionic activity

E = electromotive force in the measured sample at temperature t

E_o = the standard potential of a redox couple obtained when the activity ratio of the oxidized and reduced forms of the ionic species is one

F = the Faraday constant, 96 485 C mol^{-1}

n = number of electrons involved in a given oxidation-reduction process

m = number of protons involved in a given oxidation-reduction process

R = the molar gas constant, 8.314 Joules $mol^{-1} K^{-1}$

t = temperature in degree Celsius, and

T = the thermodynamic temperature in Kelvin of sample buffer solutions and sensors ($T = t + 273.15$).

3.2 Definitions

3.2.1 *Redox System*

A redox system is composed of oxidized and reduced ionic forms of a given solution species. It exists only if both species exist in solution, are in equilibrium and are intra-convertible by the addition or withdrawal of electrons.

An example of a typical redox system is composed of the ferric/ferrous ion couple Fe^{+++}/Fe^{++}

$$Fe^{+++} + e^- \longrightarrow Fe^{++}$$

Many redox systems incorporate protons in the equilibrium relationship; for example:

$$MnO_4^- + 5e^- + 8\,H^+ \longrightarrow Mn^{++} + 4\,H_2O$$

In cases where protons participate in the equilibrium, the redox potential is a function of the solution *p*H.

3.2.2 *Redox Potential or Oxidation-Reduction Potential (ORP)*

The redox potential is the potential measured with a suitable indicating electrode when it is immersed in a solution containing a redox system. It is a measure of the oxidation-reduction power of a solution and also an important means of determining the equilibrium state of a redox reaction and the degree of completeness of reaction procedures which employ changes in the oxidant/reductant ratio, as in potentiometric titrations. If several redox systems are present in solution, a mixed potential is observed.

The redox potential measured with an inert electrode may be related to the activities of the oxidant and reductant species by the Nernst (or Peters) equation:

$$E = E_o + \frac{RT}{nF} \quad ln \quad \frac{a_{ox}}{a_{red}}$$

Oxidation-reduction potential is often measured solely to assess a relative state of the system or for control purposes during the addition of a control reagent or reactant to a titrated sample. The qualitative behaviour of an oxidation-reduction potential system may be understood by reference to the form of the governing Nernst (or Peters) equation; it is advisable not to use the equation to make specific theoretical predictions of potentials to be observed for a given state of the systems due to the large experimental inaccuracies arising from such phenomena as junction potentials, complexation of solution species and mixed potentials observed at an oxidation-reduction electrode as a result of several oxidation-reduction potential systems existing simultaneously in the test solution.

It should be pointed out that sure there is the possibility of a variable number of electrons participating in the oxidation reduction equilibrium reaction depending on the specific reaction or reactions and solution conditions. It is not possible to compensate for the temperature dependence of the oxidation-reduction potential based on the theoretical considerations.

Redox potentials are commonly expressed by reference to a standard hydrogen electrode which by definition has a potential of zero and has no temperature coefficient of potential. Care must be taken to state the reference electrode system with which the observed redox potential is compared. Most tabulated data and theoretical computations utilize the standard hydrogen electrode; it should again be pointed out that little absolute significance is given to the absolute potential observed in practical solutions, due to the possible presence of several oxidation-reduction complexes and the *p*H dependence of the value of the ORP voltage for many frequently encountered oxidation-reduction potential systems.

When protons are involved in a redox equilibrium, the potential determining equation has the form:

$$E = E_o + \frac{RT}{nF}\left[ln \left(\frac{a_{ox}}{a_{red}}\right) + ln\,(a_{h+}) \right]$$

The ratio of the number of electrons *n* to the number of protons *m* involved in the reaction is very important in determining the sensitivity of the system to *p*H changes of the system.

3.2.3 *Reference Electrode*

The ideal reference electrode provides a known voltage which is stable and independent of the test or calibration solution composition. It is based on a reversible electrochemical system with a high exchange current density and has a potential which may be predicted by thermodynamics. It also has the property of allowing moderate amounts of measuring current to be passed through it without departure from its standard potential. Aside from the role as a quantitative comparison potential source, it has the practical value of allowing connection of the two terminal potential measuring devices back into the test solution (one input terminal is connected to the ORP sensing electrode and the other is connected to the reference electrode).

3.2.4 *Redox Electrode*

A redox electrode is a relatively inert electron conducting electrode which is used in a solution containing a redox couple system in order to determine the redox potential of the system. Typical electrode materials are platinum or gold and serve as a site for the electron exchange reactions of the redox couple.

Electrodes with a matt or dull surface on the conductive element will tend to respond more slowly to changes in redox potential than electrodes which are smooth and have a high lustre. Metallic electrodes are not truly inert and may exhibit history dependence because of oxide formation or adsorption on the surface of the electrode.

3.2.5 *Redox Calibration Solution*

An aqueous solution prepared according to a specific formula, using recognized analytical grade chemicals. The water used should have a conductivity of less than 2 µS cm $^{-1}$ and be oxygen free. The use of a redox calibration solution is in the calibration of redox analyzers in a fashion analogous to that of the use of *p*H buffers in the calibration of *p*H analyzers. Specific recommended redox calibration solutions are given in Annex A.

3.2.6 *Input Offset Voltage*

A voltage that is applied between the input terminals to obtain zero output voltage.

3.2.7 *Common Mode Input Voltage*

A voltage that is applied to both input terminals at the same time.

3.2.8 *Input Common Mode Rejection Ratio (CMRR)*

The ratio of the input voltage range to the maximum change in input offset voltage over this range.

4 PROCEDURE FOR STATEMENT

See 4 of IS 13673 (Part 1) and the following:

The manufacturer shall provide statements on the sensor unit and the electronic unit as indicated in **4.1** through **4.3**.

NOTES

1 Linearity and warm-up statements are not required for sensor units. For complete analyzers, statements on linearity and warm-up refer only to the electronic units and are validated as in IS 13673 (Part 1).

2 Errors and error limits should be stated in mV values.

4.1 Additional Statements on Sensor Units and Analyzers

4.1.1 *Composition of Electrode at which Electron Exchange Occurs*

4.2 Additional Statements on Electronic Units

4.2.1 *Rated Input Voltage Range of Use*

4.2.2 *Rated Input Offset Range*

4.2.3 *Input Resistance*

4.2.4 *Input Offset Voltage at Reference Temperature*

4.2.5 *Maximum Allowable Common Mode Input Voltage*

4.3 Statements on Electrodes

4.3.1 *Reference Electrodes*

4.3.1.1 *Resistance (including junction) at 25°C or at a specified temperature*

NOTE — The resistance may be significantly higher at lower temperature.

4.3.1.2 *Flow rate of the electrolyte at room temperature, at a given hydrostatic pressure*

4.3.1.3 *Rated range of sample temperature*

4.3.1.4 *Rated range of sample* pH*, if relevant*

4.3.1.5 *Half cell system and filling solution used*

4.3.1.6 *Rated range of sample pressure*

4.3.2 *Redox Electrodes*

4.3.2.1 *Materials of construction*

4.3.2.2 *Rated range of sample pressure*

4.3.2.3 *Rated range of sample temperature*

5 RECOMMENDED STANDARD VALUES AND RANGE OF INFLUENCE QUANTITIES AFFECTING THE PERFORMANCE OF ELECTRONIC UNITS

See 5 of IS 13673 (Part 1).

6 VERIFICATION OF VALUES

See 6 of IS 13673 (Part 1) and the following.

6.1 General Aspects

6.1.1 Compliance tests shall be performed with the apparatus ready for use (including accessories) after warm-up time and after adjustments have been made in accordance with the manufacturer's instructions.

6.1.2 During all measurements with more than one test solution, the following sensor unit treatment shall be followed, unless otherwise indicated.

The electrode pair (sensor unit) shall be carefully rinsed with deionized water; thereafter pre-rinsing with the new solution and only then may it be immersed in the beaker filled with fresh solution. The beakers shall be refilled each time in case several series of measurements are prescribed. In every case, measurements shall be made in stirred solutions.

6.1.3 Redox test solutions shall be used for all tests unless otherwise indicated. Appropriate reference solutions are detailed in Annex A.

6.2 Simulators for Testing Electronic Units

The basic function of simulators for testing electronic units used with ORP sensor units is to supply different electromotive force levels, representing known oxidant to reductant activity ratios through very high series resistors necessary for redox sensor units.

The simulator consists of a stepped voltage divider supplied by a stabilized adjustable voltage source and followed by selectable series resistors. A voltage range of ±1 500 millivolts is required.

The network should be such that the output voltage steps represent multiples (or sub-multiples in case of expanded scale electronic units) of a standard e.m.f. increment.

6.3 Test Procedures for Sensor Units and Analyzers

NOTE — In the case of special applications where these tests are not appropriate, additional test procedures may be agreed upon between manufacturer and user.

In any case, the electronic unit shall be tested, separately from the sensor unit, with a simulator as specified under **6.2**. An electronic unit which has been tested successfully in this way is referred to as an appropriate electronic unit in **6.3.2.1** and following.

6.3.1 *Operating Error*

See **6.3.6**.

6.3.2 *Repeatability*

6.3.2.1 *Sensor unit*

Using an appropriate electronic unit perform the test as indicated in **6.3.2.2**.

6.3.2.2 *Analyzer*

The sensor unit is exposed to test solutions representing as nearly as possible the minimum, the maximum and the median rated values. The steps are repeated N times (where $N > 6$) on each test solution in turn, with no rinsing between the readings, at 25°C room temperature, at intervals of about ten times the instrument's 90 percent time. The standard deviation is calculated for each set of recorded values for each solution. The mean standard deviation is calculated and reported as repeatability.

The temperature of all solutions shall be the same within ± 0.2°C and reported together with the repeatability.

The sensor unit shall be inserted into the solutions as instructed by the manufacturer.

6.3.3 *Stability*

6.3.3.1 *Sensor unit*

Using an appropriate electronic unit, perform the test as indicated in **6.3.3.2**.

6.3.3.2 *Analyzer*

This sensor unit is exposed to a test solution representing as nearly as possible the midscale rated redox value and the indicated value is recorded. This is repeated after the time interval chosen from those listed in **6.7.4** of IS 13673 (Part 1) and the stability is calculated and reported in terms of mV.

The temperature of solution and sensor unit shall be constant within ± 0.5°C and reported together with the stability.

6.3.4 *Output Fluctuation for Analyzer*

For this test, the analyzer output is to be displayed on a strip chart recorder whose response time is at least as short as that of the analyzer.

The sensor unit is exposed to a test solution representing the approximately mid-scale redox value, at any constant temperature within the rated range of sample temperature for a period of 5 min and the maximum peak-to-peak value of the random or regular deviations from the mean output is determined in terms of redox millivolt potential.

The test is repeated three times and the average of the readings is reported.

NOTE — For the purposes of this standard, spikes caused by the influence of external electromagnetic fields or by supply mains spikes are considered as due to changes in influence quantities and are therefore ignored in the determination of output fluctuation.

6.3.5 *Delay Time* (T_{10}), *Rise (Fall) Time* (T_r, T_f) 90 *percent Time* (T_{90})

These properties are defined in IS 13673(Part 1) and are usually a function of the particular application rather than the instrument and they may not be fully specified for the purposes of this standard. Therefore, it is advisable to design the test in line with the application in so far as possible.

6.3.6 *Operating Period*

The purpose of this procedure is to test the analyzer or sensor unit under worst case conditions thus substituting for complete verification of operating error. However, the test procedure is under consideration. The basic problem is to determine an appropriate test solution since the presence of varying amounts of contaminating substances (grease, proteins, bacteria, algae, etc which are previous sample exposure history of the electrode in many of the typical solutions for which this standard applies) has a substantial effect on the operating period. For this reason, the test should be agreed upon between manufacturer and user.

NOTE — The time interval for operating period should be chosen from the same list as used for stability.

6.3.7 *Effect of Sample Temperature*

This is an important parameter, but very difficult to quantify as a result of theoretical considerations. Tests should be performed under reference conditions.

6.3.8 *Effect of Sample Pressure*

For flowing junction reference electrodes, a pressure slightly positive to the stream pressure must be maintained to allow good junction flow rate and prevent back diffusion of sample in the reference electrode.

6.4 Test Procedure for Electronic Units

6.4.1 *Common Mode Rejection Ratio* (*CMRR*)

The maximum rated common mode input voltage (V_c) is applied to the electronic unit and the output reading noted. Then, using a simulator, an input voltage (V_i) is applied to the unit, of such a value that the resulting output reading equals that value previously noted.

The CMRR is calculated according to:

$$\text{CMRR} = 20 \log \frac{V_c}{V_i}$$

6.5 Test Procedures for Electrodes

6.5.1 *Resistance of Reference Electrodes*

Place the electrode to be tested and a platinum or silver wire in 3.5 mol-l^{-1} KCl solution. Apply an alternating voltage of up to 5 V with a frequency of 50 Hz or more and measure the current through the circuit. The electrode resistance can be obtained by:

$$R = \frac{E_{\text{mean}}}{I_{\text{mean}}}$$

where

E_{mean} = rms potential of the applied alternating voltage, and

I_{mean} = rms of the measured alternate current.

NOTE — The use of commercially available conductivity meters or appropriate resistance meters can also be recommended provided that they apply an alternating voltage to the external circuit.

6.5.2 *Flow Rate of Reference Electrode Electrolyte*

The test method may be selected by agreement between the manufacturer and the user. Two suitable methods are given in **6.5.2.1** and **6.5.2.2**.

The second method is particularly useful where several electrodes are to be tested simultaneously. Flow rates of less than 1 ml per day are measured by the first method. For higher rates, the second method may be used.

The first method requires the use of a high impedance voltmeter with a readability of 1 mV or less.

Differential pressure and temperature shall be constant for both methods and reported with results.

6.5.2.1 The electrode is filled with 3.5 mol-l^{-1} KCl and placed in a beaker with a known volume of distilled or doubly deionized water (approximately 20 ml) with a chloride-sensitive electrode.

The electrode pair shall stand for 72 h or more, after which read the potential in volts and solve for flow rate as follows. Determine the concentration by reading from previously prepared calibration curves. The flow rate, Q, flow per hour, is then calculated from:

$$Q = \frac{cV}{c't}$$

where

c = final chloride concentration in mol-l^{-1};

V = volume of water in beaker, in litres;

c' = chloride concentration in the reference electrode, in mol l^{-1}; and

t = test time, in hours.

6.5.2.2 The electrode is filled with KCl solution to rated level and the liquid junction is immersed in water for 72 h or more. Then the electrode is refilled to rated level again with KCl and flow rate Q is calculated from:

$$Q = \frac{V}{t}$$

where

V = volume of KCl solution for refill, in litres; and

t = test time, in hours.

6.5.3 *Insulation Resistance Effects*

Although not as critical to the measurement as in *p*H measurement, because the source impedance of a *p*H electrode is much higher than that of an ORP electrode, care should be taken to minimize loss of insulation resistance due to the choice of low resistance materials of construction for electrode bodies or electrode holders and due to condensation on the electrodes, cables and electrode holders. Removal of condensation by moderate heating and dissipation are recommended.

ANNEX A

(*Clauses* 3.2.5 *and* 6.1.3)

REDOX CALIBRATION SOLUTIONS

To check the function of an analyzer, one may employ the following test solution. The redox potentials are cited at a temperature of 25°C *vs* the standard hydrogen electrode as a reference electrode. For use with more common reference electrodes such as the silver/silver chloride or calomel (mercury/mercurous chloride) systems, one should subtract the potential of the reference electrode to be used relative to the standard hydrogen electrode from the potentials herein tabulated.

System	p*H Value*	E_H
a) Quinhydrone saturated potassium tetraoxalate (12.59 g/l) buffer	1.68	+600 mV
b) Quinhydrone saturated potassium hydrogen phthalate (10.21 g/l) buffer	4.01	+462 mV
c) Quinhydrone saturated sodium dihydrogen phosphate (6.21 g/l), disodium hydrogen phosphate (3.59 g/l) solution	7.00	+285 mV
d) Potassium ferricyanide (4.11 g/l) + Potassium ferrocyanide $3H_2O$ (5.28g/l) + Potassium dihydrogen phosphate (1.8 g/l) +Disodium Hydrogen Phosphate (3.4 g/l)	7.00	+427 mV

NOTE — The *p*H 7.0 quinhydrone-saturated solution should be freshly prepared before use because of the possibility of the oxidative degradation of the quinhydrone during storage at this *p*H.

ANNEX B

(*Informative*)

STANDARD POTENTIALS OF THE REFERENCE ELECTRODE SYSTEMS

The standard potentials of the silver/silver chloride and mercury/mercurous chloride reference electrode systems are tabulated below for various temperatures and for different internal filling solutions compositions. All potentials cited below are with reference to the standard hydrogen electrode and are expressed in millivolts.

Standard Temperature	*Mercury/Mercurous Chloride*	*Silver/Silver Chloride*			
°C	Saturated KCl	1 mKCl	3 mKCl	3.5 mKCl	Sat. KCl
0	260	249	224	222	221
5	257	247	221	219	216
10	254	249	217	215	212
15	251	241	214	212	207
20	248	239	211	209	202
25	244	236	207	204	197
30	241	233	203	200	192
35	238	230	200	195	187
40	234	227	196	191	181
45	231	224	192	187	176
50	227	221	188	182	171

NOTE — For the KCl concentrations cited above, M=mol-l^{-1} at 20°C.

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This Indian Standard has been developed from Doc : No. LTD 21 (1456).

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

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Printed at New India Printing Press, Khurja, India